Composites Science and Technology 129 (2016) 1–9

Contents lists available at ScienceDirect

Composites Science and Technology

journal homepage: http://www.elsevier.com/locate/compscitech

Graded-permittivity polymer nanocomposites as superior dielectrics

Tommaso Nardi [a], Nicolas Mora [b], Farhad Rachidi [b], Yves Leterrier [a, *]

[a] Laboratoire de Technologie des Composites et Polymères (LTC), École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland
[b] Electromagnetic Compatibility Laboratory (EMC-Lab), École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

ARTICLE INFO

Article history:
Received 17 December 2015
Received in revised form
15 March 2016
Accepted 9 April 2016
Available online 11 April 2016

Keywords:
Electrical properties
Functional composites
Nano particles

ABSTRACT

Materials exhibiting a gradient in permittivity are synthesized through the application of an external magnetic field to a suspension of Fe_3O_4@TiO_2 nanoparticles in an epoxy matrix. It is shown how the application of the magnetic field not only induces the magnetophoretic motion of the particles, but causes also their alignment in high aspect ratio structures. The combination of these two effects gives rise to graded nanocomposites exhibiting gradients in permittivity that go beyond the ones predicted for nanocomposites with homogeneously distributed and isotropic inclusions. Moreover, it is demonstrated through numerical simulations how such nanocomposites, employed as electrical insulators, can efficiently reduce the electrical field stress at the interface between the electrode and the insulator, being therefore suitable candidates as long-lasting high-voltage dielectrics.

1. Introduction

For size reduction and enhanced reliability of electric power equipment, the electric field stress around solid insulators must be considered [1]. In the case of high-voltage insulators, the insulation performance around the insulator is improved by various techniques, such as controlling the insulator shape, adding shield electrodes for electric field relaxation, or through the introduction of an embedded electrode [2]. However, these electric field management techniques lead to complicated equipment structures and increased manufacturing cost. Thus, new concepts for solid insulators emerge, which are should in principle overcome the drawbacks associated with complex configurations. Kurimoto et al. [2,3] investigated the applicability of functionally graded materials (FGM) with spatial distribution of dielectric permittivity ε (ε-FGM) to reduce electric stresses on the electrode surface in contact with solid insulating materials. Such stresses are among the key factors, which control the long-term performance of high-voltage insulators. Their results show that the lifetime of ε-FGM insulators based on epoxy and graded concentrations of TiO_2 and Al_2O_3 was up to 8.2 times higher than that of a homogeneous insulator. Previous work already showed how polymer composite FGM were efficiently synthesized through the application of an external magnetic field to a suspension of magnetic nanoparticles in a polymer matrix, prior to polymerization [4–6]. This synthetic strategy is employed in this work in order to create FGM exhibiting gradients in electrical permittivity.

First, we synthesized Fe_3O_4@TiO_2 nanoparticles (NP) with an amorphous TiO_2 shell and we increased their permittivity by inducing the partial crystallization of the shell through a calcination step. Hence, we created graded permittivity nanocomposites through the magnetophorese of high dielectric constant and magnetic Fe_3O_4@TiO_2 NP in a low-viscosity epoxy matrix. Experimental characterizations and numerical simulations demonstrated how such nanocomposites have the potential to efficiently reduce the electrical field stress at the electrode-insulator interface and deserve good attention for applications as long-lasting high-voltage electrical insulators.

2. Experimental

Materials: Titanium(IV) chloride (99.9%) was purchased from Acros. Hydrogen peroxide (30%) was purchased from Reactolab SA. The epoxy resin DER 321 was purchased from Dow whereas the hardener diethylenetriamine was purchased from Aldrich. Ammonia solution (25% min) was purchased from VWR. All products were used as received without any further purification.

Synthesis of Fe_3O_4@TiO_2 core–shell nanoparticles: To synthesize the Fe_3O_4 cores, the synthetic procedure reported by Bumb et al. was followed [7]. Briefly, $FeCl_3 \cdot 6H_2O$ (8 mmol) and $FeCl_2 \cdot 4H_2O$ (4 mmol) were dissolved in deionized water (190 ml) at room temperature by magnetic stirring in a beaker. Under conditions of vigorous stirring, 25% NH_3 (10 ml) was poured down the vortex of

* Corresponding author.
E-mail address: yves.leterrier@epfl.ch (Y. Leterrier).

http://dx.doi.org/10.1016/j.compscitech.2016.04.010
0266-3538/

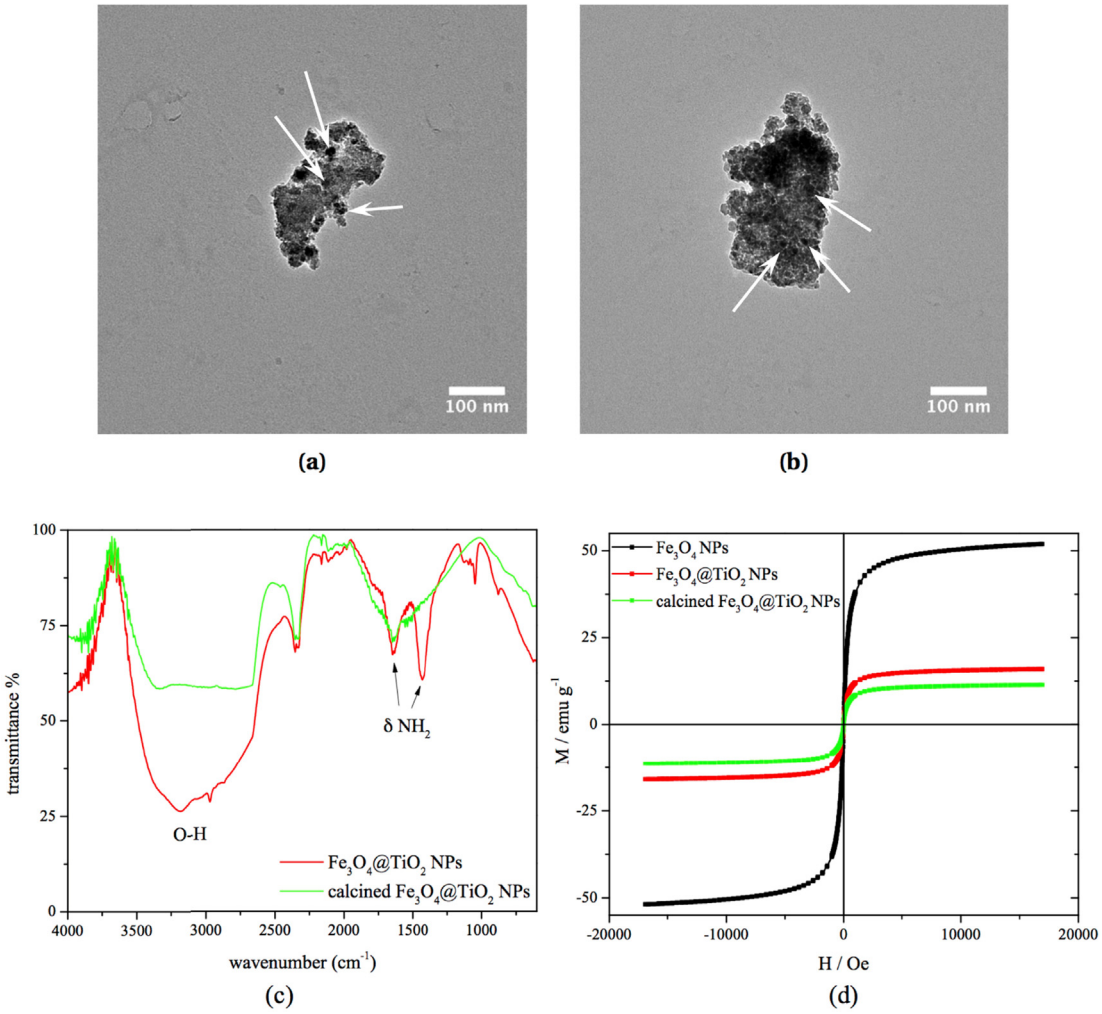

Fig. 1. TEM images of individual Fe_3O_4@TiO_2 nanoparticles with arrows pointing to several Fe_3O_4 cores before (a) and after (b) the calcination step (450 °C for 6 h), FTIR spectra of the nanoparticles before (red) and after (green) the calcination step (c) and room temperature magnetization curves of bare magnetite nanoparticles and Fe_3O_4@TiO_2 nanoparticles before and after the calcination step (d). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the iron solution. Immediately, magnetite formed a black precipitate. After stirring for 10 min, the particles were centrifuged and dispersed in of deionized water (50 ml). The as synthesized Fe_3O_4 NP were subsequently coated exploiting a synthetic procedure for TiO_2 nanoparticles reported by Buscaglia et al. [8] with minor modifications. First, $TiCl_4$ (0.7 ml) were added to the ice-cooled solution of Fe_3O_4 nanoparticles in water (50 ml). Then, a peroxotitanium complex was prepared by adding H_2O_2 (30%, 1 ml) to the above–mentioned $Fe_3O_4/TiCl_4$ solution. The pH was hence increased through the addition of aqueous ammonia (4.5 ml, 5.44 mol/L) and the solution was slowly heated to 95 °C and maintained at this temperature for 5 h. Finally, the solution was let cool down to room temperature and particles were washed and collected by centrifugation. To increase the permittivity of the as-synthesized particles, a calcination step at 450 °C for 6 h under N_2 flow (10 ml/min) was performed.

Characterization: The NP morphology was characterized using a Philips/FEI CM12 transmission electron microscope (TEM) at an accelerating voltage of 120 kV. Typically, few drops of diluted NP suspensions (in cyclohexane for Fe_3O_4 NP, in ethanol for Fe_3O_4@-TiO_2 NP) were deposited on carbon filmed copper grids (200 mesh, Plano GmbH). Fourier Transform Infrared (FTIR) spectra were acquired using a Perkin Elmer Spectrum One MIR (600–4000 cm^{-1}) with an attenuated total reflectance (ATR) accessory. The spectra were acquired with 32 scans and a resolution of 4 cm^{-1}. Magnetization loops of Fe_3O_4@TiO_2 core–shell NP in powder form were measured at T = 295 K by means of a Vibrating Sample magnetometer (VSM) operating in the ±15 kOe field range and equipped with a liquid–N_2 continuous-flow cryostat. X-ray powder diffraction (XRPD) data for qualitative and quantitative phase analysis were collected using a Bragg–-Brentano θ–2θ diffractometer (Philips PW1729 PANalytical, Netherlands) equipped with a gas proportional detector. The radiation source was an X–ray tube with copper radiation (λ Cu $K_{\alpha 1}$ = 1.54059 Å) and the anode tube load was 40 kV and 35 mA. The samples were loaded on a quartz flat holder in order to have a zero background. XRPD patterns, both for the phase composition and the structural characterization, were collected at room temperature in the 15–135° 2θ range, with a scanning rate of 0.004°s^{-1} and a step size of 0.02° 2θ. Preliminary qualitative phase analyses were performed using the X'Pert High Score Plus software (PANalytical, Netherlands). In order to determine the amorphous phase content of each powder, pure α-Fe_2O_3 was chosen as internal standard. Mixed samples were prepared diluting original samples with 10 wt% of hematite. The internal standard hematite (α-Fe_2O_3) was refined against the standard reference Si powder